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PART XIX

VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES

PART XIX. MASS SPECTROMETRIC DETERMINATION OF THE DISSOCIATION ENERGY OF THE MOLECULES Sc_2, Y_2, La_2 AND YLa

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FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF61(052)-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001, "Non-Graphitic." The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio. Mr. F. W. Vahldiek was the project engineer.

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ABSTRACT

The diatomic molecules Sc_2, Y_2, La_2 and YLa have been identified mass spectrometrically in the vapors above condensed scandium, yttrium, lanthanum and Y-La alloys respectively. Their dissociation energies are $D_0^\circ(Sc_2) = 25.9 \pm 5$, $D_0^\circ(Y_2) = 37.3 \pm 5$, $D_0^\circ(La_2) = 57.6 \pm 5$ and $D_0^\circ(YLa) = 47.3 \pm 5$ kcal/mole.

This technical documentary report has been reviewed and is approved.

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MASS SPECTROMETRIC DETERMINATION OF THE

DISSOCIATION ENERGY OF THE MOLECULES Sc_2, Y_2, La_2 and YLa*

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Although classical chemistry, spectroscopy[1], and mass spectrometry[2] have **succeeded** in identifying about 30 homonuclear diatomic molecules,those of the "true" transition elements, i.e. those with unfilled d shells, were as yet unidentified. A recent survey of heats of vaporization of elements and dissociation energies of known homonuclear diatomic molecules indicated that the transition elements of the molecules Sc_2, Y_2 and La_2 should be the more easily detectable[3] under usual experimental conditions in a mass spectrometer[2].

Samples of metallic Sc, Y and La were therefore vaporized from Ta , Mo or W Knudsen cells. The effusing vapors were ionized by electron impact and subsequently mass analyzed[2,4].

At temperatures where the effective pressure ranged from 10^{-5} to 5 10^{-3} atm small peaks due to Sc_2^+, Y_2^+ and La_2^+ ions were observed. Their intensity profile indicated the neutral precursor to originate from the Knudsen cell. Because of the low intensities,only qualitative ionization efficiency curves could be obtained, which indicate however that the approximate ionization potentials of these molecules are slightly lower than those of the

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corresponding atoms[5]. To avoid the possible interference of charge exchange $Me^{++} + X \rightarrow Me^{+} + X^{+}$ which can give peaks at an apparent mass $2Me^{+}$[6], and fragmentation of Me_2O and Me_2O_2 molecules which were present in small concentration in the vapor the measurements were made with 12 eV electrons. It was further estimated that ion attachment reactions $Me^{+} + Me \rightarrow Me_2^{+}$ possibly occurring in two or three body collisions in the source are unlikely to affect the measured Me_2^{+} intensities.

Dissociation energies of Sc_2, Y_2, La_2 and YLa were calculated by the absolute entropy method. Pressure independent reactions $Me_2(g) \rightarrow Me(g) + Me(s)$ were considered using $L_0^o(Y) = 97.6$[7] and $L_0^o(La) = 104.1$[7] kcal/mole. Since all crucible materials (Ta, Mo, W) gave rise to pronounced alloy formation with liquid Sc, pressure measurements based on the Hertz-Knudsen relation were made[2,4] for this element. For gaseous Sc, Y and La, the free energy functions are those given by Stull and Sinke[8]. For consistency, those for condensed Y and La were taken from the same source as the heats of sublimation[7]. The free energy functions of Sc_2, Y_2 and La_2 were calculated[8] using an effective quantum weight of 5, a vibration frequency of 230 cm^{-1} (estimated by analogy with molecules of similar stability and molecular weight) and 2.70, 2.80 and 2.80 Å respectively as interatomic distance (obtained from Badger's rule[9]). For YLa the values of Y_2 and La_2 were averaged and corrected for the absence of symmetry. The numerical values (in cal/deg.mole) for Sc_2, Y_2, La_2 and YLa are respectively 68.3, 72.3, 74.1 and 74.6 at 2000°K and 69.6, 73.6, 75.4 and 76.0 at 2300°K. Table 1 summarizes the data and results.

The dissociation energies of Sc_2, Y_2 and La_2 are of the same magnitude as those of Cu_2, Ag_2 and Au_2 : 45.5, 37.6 and 51.5 kcal/mole[4] respectively, and seem as for the latter molecules[4] to be related to the availability of low-lying excited states of the atoms.

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TABLE 1

Mole-cule	Equilibrium	T°K	$\log I_1/I_2$ (a)	logK	ΔH°_0 kcal/mole	D° kcal/mole
Sc_2	$Sc_2(g) \rightarrow 2Sc(g)$	2097	4.94	2.66	25.8	25.9±5
		2152	5.04	2.90	24.1	
		2165	4.92	2.67	26.6	
		2000	4.67	2.39	27.0	
		2001	4.68	2.50	26.0	
		1999	4.56	2.25	28.2	
				mean:	25.9	
Y_2	$Y_2(g) \rightarrow Y(g) + Y(s,1)$	2300	4.82	4.82	-60.9	37.3±5
		2286	4.69	4.69	-59.3	
		2304	4.58	4.58	-58.5	
		2315	4.80	4.80	-61.0	
		2248	4.99	4.99	-61.6	
		2271	4.84	4.84	-60.5	
				mean:	-60.3	
La_2	$La_2(g) \rightarrow La(g) + La(1)$	1998	4.14	4.19	-47.3	57.6±5
		2003	4.23	4.28	-48.2	
		1945	3.85	3.90	-43.8	
		1998	3.87	3.92	-44.8	
		2065	3.80	3.85	-45.3	
		2161	3.46	3.51	-43.3	
		2154	3.42	3.47	-43.9	
		2185	3.64	3.69	-45.3	
		2091	3.79	3.84	-45.5	
		2102	4.08	4.13	-48.5	
		2117	3.92	3.97	-47.3	
		2070	3.83	3.88	-45.7	
		2055	4.11	4.16	-48.1	
		2190	3.86	3.91	-47.8	
		2180	3.79	3.84	-47.0	
		2159	3.78	3.83	-46.5	
		2128	3.82	3.87	-46.5	
		2304	3.74	3.79	-48.2	
		2274	3.66	3.71	-47.1	
		2274	3.84	3.89	-48.9	
		2307	3.66	3.71	-47.4	
		2316	3.73	3.78	-48.3	
		2295	3.63	3.68	-46.7	
		2311	3.24	3.29	-43.1	
				mean:	-46.5	

TABLE 1 (cont.)

Molecule	Equilibrium	T°K	logK	ΔH_0^o kcal/mole	D_0^o kcal/mole
YLa	$YLa(g)+La(g)->Y(g)+La_2(g)$	2307	0.46	-10.2	48.0
		2316	0.51	-10.8	
		2295	0.50	-10.6	
		2311	0.30	- 8.5	
		2299	0.31	- 8.6	
		2220	0.49	-10.1	
		2211	0.35	- 8.5	
			mean:	- 9.6	
	$YLa(g)+Y(g)->La(g)+Y_2(g)$	2262	-0.91	8.6	45.6
		2248	-0.85	8.1	
		2290	-0.89	8.2	
			mean:	8.3	
	$2YLa(g)->Y_2(g)+La_2(g)$	2186	-0.47	- 0.9	47.0
			mean:		47.3±5

(a) $\log P_1/P_2 = \log(I_1/I_2)\ (\sigma\gamma_2/\sigma\gamma_1)$; σ_2/σ_1 = ratio of ionization cross sections $\simeq$ 1.6 ; γ_2/γ_1 = ratio of secondary electron multiplier yields.